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FILE 'CAPLUS' ENTERED AT 15:25:49 ON 13 MAY 2004

E JACOBSON ERIC/AU

E JACOBSEN ERIC/AU

L1 220 S E6-E7

E TOKUNAGA MAKOTO/AU

L2 55 S E3

E LARROW JAY/AU

L3 19 S E4-E5

L4 277 S L1 OR L2 OR L3

L5 39 S L4 AND KINETIC(W)(RESOLUTION OR RESOLN)

L6 0 S L5 AND SILYL(W)AZIDE

L7 0 S KINETIC(L)(RESOLUTION OR RESOLN) AND SILYL(W)AZIDE

L8 64 S KINETIC(L)(RESOLUTION OR RESOLN) AND AZIDE

L9 2 S L8 AND CHIRAL(W)CATALYST

=>

=> d 1-2 bib abs

L9 ANSWER 1 OF 2 CAPLUS COPYRIGHT 2004 ACS on STN  
 AN 1999:722857 CAPLUS  
 DN 131:350871

TI Chiral non-racemic catalysts containing Main-group metals and tridentate or tetradeinate ligands for asymmetric nucleophilic addition reactions to  $\pi$  bonds

IN Jacobsen, Eric N.; Sigman, Matthew S.  
 PA President and Fellows of Harvard College, USA  
 SO PCT Int. Appl., 90 pp.

CODEN: PIXXD2

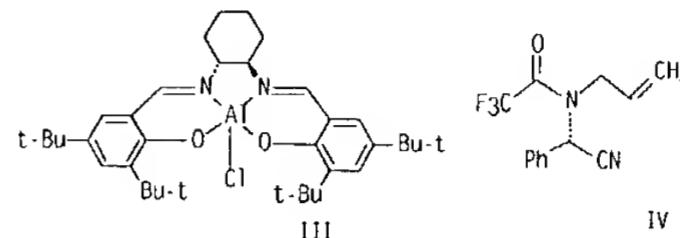
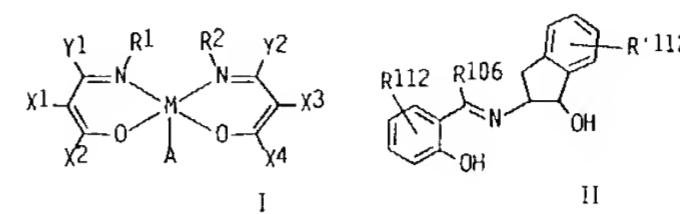
DT Patent

LA English

FAN.CNT 1

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
WO 9956699	A2	19991111	WO 1999-US9570	19990430
WO 9956699	A3	20000518		
W: CA, JP RW: AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE				
US 6521561	B1	20030218	US 1998-71842	19980501
CA 2329316	AA	19991111	CA 1999-2329316	19990430
EP 1073613	A2	20010207	EP 1999-922765	19990430
R: AT, BE, CH, DE, DK, ES, FR, GB, GR, IT, LI, LU, NL, SE, MC, PT, IE, FI				
JP 2002513734	T2	20020514	JP 2000-546729	19990430
US 2003187249	A1	20031002	US 2002-325592	20021220
PRAI US 1998-71842	A	19980501		
WO 1999-US9570	W	19990430		
OS CASREACT 131:350871: MARPAT 131:350871				
GI				

L9 ANSWER 1 OF 2 CAPLUS COPYRIGHT 2004 ACS on STN (Continued)



AB The present invention relates to a method and catalysts for the stereoselective addition of a nucleophile to a reactive  $\pi$ -bond of a substrate. Claimed is a stereoselective nucleophilic addition reaction of a  $\pi$ -bond-containing substrate with a nucleophile in the presence of a chiral, non-racemic catalyst to produce a stereoisomerically enriched addition product. The substrate comprises a C-C or C-heteroatom  $\pi$ -bond, and the nucleophile comprises at least one pair of Lewis basic electrons. The chiral, non-racemic catalysts of the invention constitute the first examples of catalysts for nucleophilic addns. that comprise a Main-group metal and a tri- or tetradeinate ligand. One of a number of preferred chiral non-racemic catalysts of the invention includes metallosalenates I (R1, R2, Y1, Y2, X1-X4 = H, halo, alkyl, alkenyl, alkyne, OH, alkoxy, siloxy, amino, nitro, SH, amines, imines, amides, phosphonates, phosphines, carbonyls, carboxyls, silyls, ethers, thioethers, sulfonyls, selenoethers, ketones, aldehydes, esters, etc., or any two or more taken together form a 4-8 membered carbocycle or heterocycle which may be a fused ring, with a proviso that requires the  $\beta$ -imincarbonyls as tetradeinate ligand). Other preferred chiral non-racemic catalysts of the invention include various metalloporphyrinates or porphyrin-like complexes, complexes of the tridentate chiral Schiff base ligand II (R106 = H, halo, alkyl, etc.; each R112, R'112 is absent or represents one or more covalent substitutions of the heterocycle to which it is attached), or complexes of various tetradeinate azamacrocycles. Catalysts may contain a Main-group metal selected from Groups 1, 2, 12, 13, or 14 of the periodic table. The catalyst may be immobilized on an insol. matrix. The nucleophilic addition reaction may be enantioselective, diastereoselective, or a

L9 ANSWER 1 OF 2 CAPLUS COPYRIGHT 2004 ACS on STN (Continued)

diastereoselective reaction which is a kinetic resoln.

The  $\pi$ -bond-contg. substrate may include, e.g., aldehydes, conjugated enals, thioaldehydes, conjugated thioenals, selenoaldehydes, conjugated selenoenals, ketones, conjugated enones, thioketones, conjugated thioenones, selenoketones, conjugated selenoenones, imines, oximes, hydrazones, glyoxylates, pyruvates, conjugated enoates,  $\alpha,\beta$ -unsatd. amides,  $\alpha,\beta$ -unsatd. imides, lactones, thionolactones, thiolactones, dithiolactones, lactams, and thiolactams. The reacting nucleophiles may include conjugate bases of weak Brønsted acids, e.g., cyanide, azide, isocyanate, thiocyanate, alkoxide, thioalkoxide, carboxylate, thiocarboxylate, and carbanions. A highly enantioselective hydrocyanation reaction is achieved by this method. Treatment of N-allylbenzaldimine with HCN in the presence of chiral (salen)Al(III) complex III (toluene, -70°, 15 h) followed by workup with TFAA affords (S)-(-)-trifluoroacetamide IV in 91% yield, 95% ee. The asym. Strecker-type reaction catalyzed by III provides a straightforward entry into enantiomERICALLY enriched  $\alpha$ -amino acid derivs. Also claimed are chiral catalysts comprising a main-group metal atom or ion, and an asym. tetradeinate or tridentate ligand wherein the catalyst catalyzes at least one asym. reaction. The asym. reactions may comprise epoxidn., aziridination, cycloaddn., sigmatropic rearrangement, addn. of nucleophiles to  $\pi$  bonds, ring-opening reactions, hetero-Diels-Alder or hetero-ene reactions, Claisen rearrangements, carbonyl redns., and addn. of nucleophiles to carbonyl groups or to C:N  $\pi$  bonds.

L9 ANSWER 2 OF 2 CAPLUS COPYRIGHT 2004 ACS on STN

AN 1999:468087 CAPLUS

DN 131:129576

TI Stereoselective epoxy ring opening reactions using chiral transition metal-salen complexes

IN Jacobsen, Eric N.; Leighton, James L.; Martinez, Luis E.

PA President and Fellows of Harvard College, USA

SO U.S., 45 pp.

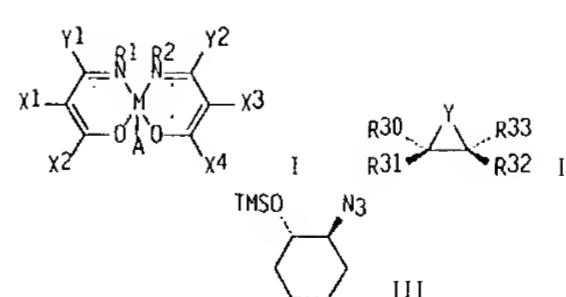
CODEN: USXXAM

DT Patent

LA English

FAN.CNT 4

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
US 5929232	A	19990727	US 1996-622549	19960325
US 5665890	A	19970909	US 1995-403374	19950314
CA 2213007	AA	19960919	CA 1996-2213007	19960314
US 6262278	B1	20010717	US 1998-134393	19980814
US 2002032338	A1	20020314	US 2001-899516	20010705
US 6448414	B2	20020910		
US 2003139614	A1	20030724	US 2002-206143	20020726
US 2004044233	A1	20040304	US 2003-615501	20030707
PRAI US 1995-403374	A2	19950314		
US 1996-622549	A2	19960325		
US 1998-134393	A1	19980814		
US 2001-899516	A1	20010705		
US 2002-206143	A1	20020726		
OS CASREACT 131:129576: MARPAT 131:129576				
GI				



AB The present invention relates to a kinetic resolution process for stereoselective or regioselective chemical synthesis which generally comprises reacting a nucleophile and a chiral or prochiral cyclic substrate in the presence of a non-racemic chiral catalyst to produce a stereoisomerically or regioselectively enriched product. Said chiral catalyst comprises an asym. tetradeinate ligand complexed with a metal atom, which complex has a

L9 ANSWER 2 OF 2 CAPLUS COPYRIGHT 2004 ACS on STN (Continued)  
rectangular planar or rectangular pyramidal geometry, e.g. metal-salen  
complexes (I: R1, R2, Y1, Y2, X1, X2, X3, X4 = hydrogen, halogen, alkyl,  
alkenyl, alkynyl, hydroxyl, amino, nitro, thiol, amines, imines, amides,  
phosphoryls, phosphonates, phosphines, carbonyls, carboxyls, silyls,  
ethers, thioethers, sulfonyls, seleno ethers, ketones, aldehydes, esters,  
or  $(CH_2)_m R_7$ , or any two or more of the substituents taken together form a  
carbocycle or heterocycle ring having from 4 to 8 atoms in the ring  
structure; wherein R7 = aryl, cycloalkyl, cycloalkenyl, heterocycle,  
polycycle; m = 0 or an integer in the range of 1 to 8; M = the late  
transition metal; A = a counterion or a nucleophile; provisos given). The  
substrates are epoxides, thioperoxides, aziridines, or cyclopropanes  
represented by general formula [II: Y = O, S, NR50, C(R52)(R54), A-B-C;  
wherein R50 = hydrogen, alkyl, carbonyl-substituted alkyl,  
carbonyl-substituted aryl, a sulfonate; R52, R54 = an electron-withdrawing  
group; A, C = absent, C1-5 alkyl, O, S, carbonyl, or NR50; B = carbonyl,  
thiocarbonyl, phosphoryl, sulfonyl; R30, R31, R32, R33 = org. or inorg.  
substituent which form a covalent bond with the C1 or C2 carbon atoms of  
1-8, and which permit formation of a stable ring structure including Y].  
Thus, cyclohexene oxide was added to a mixt. of chromium-salen complex,  
(R,R)-[1,2-bis(3,5-di-tert-butylsalicylideneamino)cyclohexane]-chromium  
(III) chloride (prepn. given) (2 mol%), and Et2O and stirred for 15 min.  
followed by adding Me3SiN3. The resulting brown soln. was stirred at room  
temp. for 28 h to give 80% 2-azidocyclohexanol (III) of 94% ee.

RE.CNT 38 THERE ARE 38 CITED REFERENCES AVAILABLE FOR THIS RECORD  
ALL CITATIONS AVAILABLE IN THE RE FORMAT

=> s 18 and catalyst  
655601 CATALYST  
659980 CATALYSTS  
839866 CATALYST  
(CATALYST OR CATALYSTS)

L10 20 L8 AND CATALYST

=> s 110 not 19  
L11 18 L10 NOT L9

=> d 1-18 bib abs

L11 ANSWER 1 OF 18 CAPLUS COPYRIGHT 2004 ACS on STN  
 AN 2004:270944 CAPLUS  
 TI Enzymatic dynamic kinetic resolution of epihalohydrins  
 AU Lutje Spelberg, Jeffrey H.; Tang, Lixia; Kellogg, Richard M.; Janssen, Dick B.  
 CS Groningen Biomolecular Sciences and Biotechnology Institute, Department of Biochemistry, University of Groningen, Groningen, 9747 AG, Neth.  
 SO Tetrahedron: Asymmetry (2004), 15(7), 1095-1102  
 CODEN: TASYE3; ISSN: 0957-4166  
 PB Elsevier Science B.V.  
 DT Journal  
 LA English  
 AB The haloalc. dehalogenase from Agrobacterium radiobacter AD1 catalyzes the reversible ring closure of vicinal haloalcs. to produce epoxides and halides. In the ring opening of epoxides, non-halide nucleophiles such as N3- are accepted. The enantioselective irreversible ring opening of an epihalohydrin by N3-, combined with racemization caused by a reversible ring opening by a halide, resulted in an enzymic dynamic kinetic resolution yielding optically active (S)-1-azido-3-halo-2-propanol. With epichlorohydrin as a substrate, the rate of ring opening by N3- was higher than the rate of racemization, resulting in a mixed kinetic resolution and dynamic kinetic resolution. With epibromohydrin as the substrate, the racemization rate was higher than the rate of ring opening, resulting in an efficient dynamic kinetic resolution. By optimizing the pH of the medium and the concns. of N3- and Br-, the product (S)-1-azido-3-bromo-2-propanol could be obtained in 84% yield and 94% ee. An (R)-enantiomer selective ring closure of this bromoalc., catalyzed by the same enzyme, caused a simultaneously occurring kinetic resolution, yielding when the conversion progressed, an increase in enantiopurity of (S)-1-azido-3-bromo-2-propanol to >99% ee with a yield of 77%. This compound and the ring-closed product glycidyl azide can be used as chiral synthetic building blocks.  
 RE.CNT 18 THERE ARE 18 CITED REFERENCES AVAILABLE FOR THIS RECORD  
 ALL CITATIONS AVAILABLE IN THE RE FORMAT

L11 ANSWER 2 OF 18 CAPLUS COPYRIGHT 2004 ACS on STN  
 AN 2004:56131 CAPLUS  
 DN 140:259747  
 TI Secondary Deuterium Kinetic Isotope Effect for Aquation, Solvolysis, and Isomerization Reactions of trans-[Co(en)2(OSMe2)N3]2+, and the Resolution of a Mechanistic Anomaly  
 AU Jackson, W. G.  
 CS School of Physical Environmental and Mathematical Sciences, Chemistry, University College (UNSW), Australian Defence Force Academy, Canberra, 2600, Australia  
 SO Inorganic Chemistry (2004), 43(8), 2577-2584  
 CODEN: INOCAJ; ISSN: 0020-1669  
 PB American Chemical Society  
 DT Journal  
 LA English  
 AB The two closely spaced NH signals in the 1H NMR spectrum of trans-[Co(en)2(OSMe2)(N3)]2+ have been reassigned using 2D NMR and other techniques. Thus, the unusual syn to anti (to Co-N3) NH rearrangement on base catalyzed substitution of the selectively deuterated complex in ND3(1) has been reinterpreted as "normal", with inversion of the effective deprotonation site accompanying the act of substitution. The re-examination of this system required a repeat study of the secondary isotope effect for the acid hydrolysis reaction, previously used to assign syn and anti amine sites, and this has been extended to other solvents (Me2SO, MeCN). The relative NH proton exchange rates are also reconsidered. A systematic rate reduction for Me2SO substitution is observed for deuterium incorporation into the cis-NH centers, irresp. of whether these are syn or anti, and the effect is much greater in Me2SO than in water. The results are interpreted in terms of zero point energy effects and coupled vibrations.  
 RE.CNT 26 THERE ARE 26 CITED REFERENCES AVAILABLE FOR THIS RECORD  
 ALL CITATIONS AVAILABLE IN THE RE FORMAT

L11 ANSWER 3 OF 18 CAPLUS COPYRIGHT 2004 ACS on STN  
 AN 2003:867324 CAPLUS  
 DN 140:93659  
 TI CrIII(salen) impregnated on silica for asymmetric ring opening reactions and its recovery via desorption/re-impregnation  
 AU Dioos, Bart M. L.; Jacobs, Pierre A.  
 CS Centre for Surface Chemistry and Catalysis, K.U. Leuven, Heverlee, 3001, Belg.  
 SO Tetrahedron Letters (2003), 44(49), 8815-8817  
 CODEN: TELEAY; ISSN: 0040-4039  
 PB Elsevier Science B.V.  
 DT Journal  
 LA English  
 AB The impregnation of CrIII(salen) complexes on silica resulted in a heterogeneous catalyst for the asym. ring opening (ARO) reaction of epoxides with good selectivity and acceptable activity. As became apparent from a series of 10 successive batch tests in the ARO reaction of 1,2-epoxyhexane, leaching was limited, while catalytic activity and selectivity were acceptable. Though the support suffered from abrasion in the batch reactor, 80% of the catalyst was easily recoverable via simple extraction from the used solid catalyst and entirely transferable onto a fresh carrier via impregnation. It was shown that 80% of the leached catalyst at the end of the tests could be transformed into a fresh heterogeneous catalyst as well.  
 RE.CNT 11 THERE ARE 11 CITED REFERENCES AVAILABLE FOR THIS RECORD  
 ALL CITATIONS AVAILABLE IN THE RE FORMAT

L11 ANSWER 4 OF 18 CAPLUS COPYRIGHT 2004 ACS on STN  
 AN 2002:502361 CAPLUS  
 DN 137:384429  
 TI Exploration of the biocatalytic potential of a halohydrin dehalogenase using chromogenic substrates  
 AU Lutje Spelberg, Jeffrey H.; Tang, Lixia; van Gelder, Marc; Kellogg, Richard M.; Janssen, Dick B.  
 CS Groningen Biomolecular Sciences & Biotechnology Institute, Department of Biochemistry, University of Groningen, Groningen, 9747 AG, Neth.  
 SO Tetrahedron: Asymmetry (2002), 13(10), 1083-1089  
 CODEN: TASYE3; ISSN: 0957-4166  
 PB Elsevier Science Ltd.  
 DT Journal  
 LA English  
 AB Halohydrin dehalogenases are bacterial enzymes that catalyze the reversible formation of epoxides from vicinal halohydrins. A spectrophotometric assay for halohydrin dehalogenases based on the absorption difference between the halohydrin para-nitro-2-bromo-1-phenylethanol and the epoxide para-nitrostyrene oxide was developed. The enantioselectivity of ring-closure reactions catalyzed by three different halohydrin dehalogenases could be estimated from the shape of progress curves. Evaluation of ring-opening reactions catalyzed by halohydrin dehalogenase from Agrobacterium radiobacter AD1 established that, in addition to Cl- and Br-, nucleophiles such as N3-, CN-, and NO2- are also accepted for the ring opening of para-nitrostyrene oxide. The ring-opening reactions with these nucleophiles resulted in highly enantioselective kinetic resolutions, which expands the scope of synthetically valuable conversions catalyzed by a halohydrin dehalogenase.  
 RE.CNT 24 THERE ARE 24 CITED REFERENCES AVAILABLE FOR THIS RECORD  
 ALL CITATIONS AVAILABLE IN THE RE FORMAT

L11 ANSWER 5 OF 18 CAPLUS COPYRIGHT 2004 ACS on STN

AN 2001:27682 CAPLUS

DN 134:208005

TI Synthesis of (-)-Astrogorgiadiol

AU Taber, Douglass F.; Malcolm, Scott C.

CS Department of Chemistry and Biochemistry, University of Delaware, Newark, DE, 19716, USA

SO Journal of Organic Chemistry (2001), 66(3), 944-953

CODEN: JOCEAH; ISSN: 0022-3263

PB American Chemical Society

DT Journal

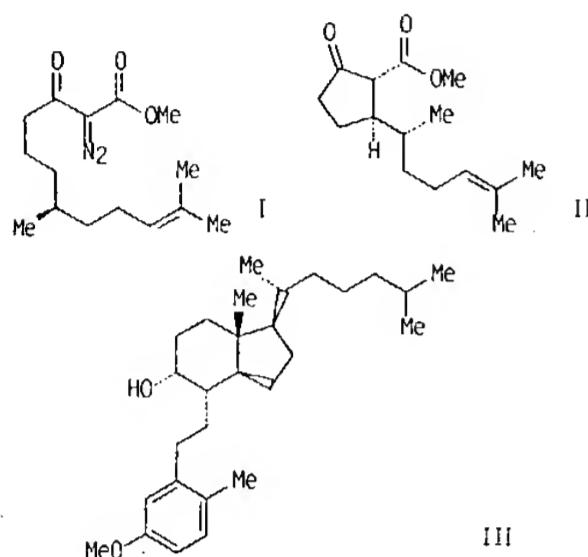
LA English

OS CASREACT 134:208005

GI

L11 ANSWER 5 OF 18 CAPLUS COPYRIGHT 2004 ACS on STN  
ALL CITATIONS AVAILABLE IN THE RE FORMAT

(Continued)



AB Reaction of Rh2(S)-PTPA4 with the (R)-citronellol-derived α-diazo-β-ketoester I led to the formation of cyclic β-ketoester II in 95% yield and 48% diastereomeric excess. The purity of II was increased to >99% de after one crystallization. To demonstrate its utility in steroid total synthesis, the β-ketoester II was carried on to secoesteroid (-)-astrogorgiadiol (III), a naturally occurring vitamin D analog with antiproliferative properties.

RE.CNT 32 THERE ARE 32 CITED REFERENCES AVAILABLE FOR THIS RECORD

L11 ANSWER 6 OF 18 CAPLUS COPYRIGHT 2004 ACS on STN

AN 2000:866575 CAPLUS

DN 134:178304

TI Highly enantioselective and regioselective biocatalytic azidolysis of aromatic epoxides

AU Speilberg, Jeffrey H.; Lutje van Hekkama Vlieg, Johan E. T.; Tang, Lixia; Janssen, Dick B.; Kellogg, Richard M.

CS Department of Biochemistry, Groningen Biomolecular Sciences and Biotechnology Institute and Department of Organic and Molecular Inorganic Chemistry, University of Groningen, Groningen, 9747 AG, Neth.

SO Organic Letters (2001), 3(1), 41-43

CODEN: ORLEF7; ISSN: 1523-7060

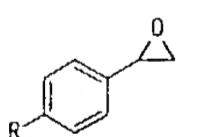
PB American Chemical Society

DT Journal

LA English

OS CASREACT 134:178304

GI



AB The halohydrin dehalogenase from Agrobacterium radiobacter AD1 catalyzed the highly enantioselective and β-regioselective azidolysis of (substituted) styrene oxides I (R = NO<sub>2</sub>, Cl, H). By means of kinetic resolutions, the remaining epoxide and the formed azido alc. could be obtained in very high ee. In a large scale conversion, the decrease in yield and selectivity due to the uncatalyzed chemical side reaction could be overcome by slow addition of azide.

RE.CNT 6 THERE ARE 6 CITED REFERENCES AVAILABLE FOR THIS RECORD  
ALL CITATIONS AVAILABLE IN THE RE FORMAT

L11 ANSWER 7 OF 18 CAPLUS COPYRIGHT 2004 ACS on STN

AN 2000:374233 CAPLUS

DN 133:135388

TI First synthesis and resolution of a planar-chiral tetrahydroindolyl complex of iron: Electronic tuning of reactivity and enantioselective nucleophilic catalysis

AU Sugimoto, Michinori; Fu, Gregory C.

CS Department of Chemistry, Massachusetts Institute of Technology, Cambridge, MA, USA

SO Chirality (2000), 12(5/6), 318-324

CODEN: CHRLEP; ISSN: 0899-0042

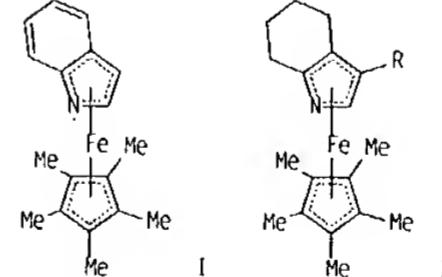
PB Wiley-Liss, Inc.

DT Journal

LA English

OS CASREACT 133:135388

GI



AB The 1st examples of an (η<sub>5</sub>-indolyl)iron complex (I) and (η<sub>5</sub>-tetrahydroindolyl)iron complexes (II: R = H (3), NMe<sub>2</sub> (5)) are described. Reactivity studies establish that the (η<sub>5</sub>-tetrahydroindolyl)iron complexes are the most active azaferrocene-derived nucleophilic catalysts reported to date and that the reactivity of these complexes can be electronically tuned. Use of planar-chiral, enantiopure (η<sub>5</sub>-3-(dimethylamino)tetrahydroindolyl)FeCp\* ((-)-5 or (+)-5) in asym. catalysis leads to stereoselectivities comparable to those furnished by a previously described azaferrocene complex.

RE.CNT 29 THERE ARE 29 CITED REFERENCES AVAILABLE FOR THIS RECORD  
ALL CITATIONS AVAILABLE IN THE RE FORMAT

L11 ANSWER 8 OF 18 CAPLUS COPYRIGHT 2004 ACS on STN  
 AN 2000:316228 CAPLUS  
 DN 133:30382

TI Asymmetric Catalysis of Epoxide Ring-Opening Reactions  
 AU Jacobsen, Eric N.  
 CS Department of Chemistry and Chemical Biology, Harvard University, Cambridge, MA, 02138, USA  
 SO Accounts of Chemical Research (2000), 33(6), 421-431  
 CODEN: ACHRE4; ISSN: 0001-4842  
 PB American Chemical Society  
 DT Journal: General Review  
 LA English  
 AB A review with 37 refs. The discovery of the metal salen-catalyzed asym. ring-opening (ARO) of epoxides is chronicled. A screening approach was adopted for the identification of catalysts for the addition of TMSN<sub>3</sub> to meso-epoxides, and the chiral (salen)CrN<sub>3</sub> complex was identified as optimal. Kinetic and structural studies served to elucidate the mechanism of catalysis, which involves cooperative activation of both epoxide and azide by two different metal centers. Covalently linked bimetallic complexes were constructed on the basis of this insight, and shown to catalyze the ARO with identical enantioselectivity but 1-2 orders of magnitude greater reactivity than the monomeric analogs. Extraordinarily high selectivity is observed in the kinetic resolution of terminal epoxides using the (salen)CrN<sub>3</sub>/TMSN<sub>3</sub> system. A search for a practical method for the kinetic resolution reaction led to the discovery of highly enantiomer-selective hydrolytic ring-opening using the corresponding (salen)Co<sup>III</sup> catalyst. This system displays extraordinary substrate generality, and allows practical access to enantiopure terminal epoxides on both laboratory and industrial scales.

RE.CNT 50 THERE ARE 50 CITED REFERENCES AVAILABLE FOR THIS RECORD  
 ALL CITATIONS AVAILABLE IN THE RE FORMAT

L11 ANSWER 9 OF 18 CAPLUS COPYRIGHT 2004 ACS on STN  
 AN 1999:753800 CAPLUS  
 DN 132:151334

TI The first chiral diimido chelate complexes of molybdenum and tungsten: transition metal diimido complexes on the way to asymmetric catalysis  
 AU Kretzschmar, Eike A.; Kipke, Jennifer; Sundermeyer, Jorg  
 CS Fachbereich Chemie, Philipps-Universität Marburg, Marburg, D-35032, Germany  
 SO Chemical Communications (Cambridge) (1999), (23), 2381-2382  
 CODEN: CHCOFS; ISSN: 1369-7345  
 PB Royal Society of Chemistry  
 DT Journal  
 LA English  
 AB The first complexes [M(TADDAMINat)Cl<sub>2</sub>(dme)] [M = Mo (2), W (4)] containing a chiral diimido ligand regime have been synthesized; 2 has been structurally characterized and used as catalyst for C-C and C-N bond formation reactions.

RE.CNT 21 THERE ARE 21 CITED REFERENCES AVAILABLE FOR THIS RECORD  
 ALL CITATIONS AVAILABLE IN THE RE FORMAT

L11 ANSWER 10 OF 18 CAPLUS COPYRIGHT 2004 ACS on STN  
 AN 1999:655145 CAPLUS  
 DN 132:35320

TI Chromium catalyzed kinetic resolution of 2,2-disubstituted epoxides  
 AU Lebel, Helene; Jacobsen, Eric N.  
 CS Department of Chemistry and Chemical Biology, Harvard University, Cambridge, MA, 02138, USA  
 SO Tetrahedron Letters (1999), 40(41), 7303-7306  
 CODEN: TELEAY; ISSN: 0040-4039  
 PB Elsevier Science Ltd.  
 DT Journal  
 LA English  
 OS CASREACT 132:35320  
 AB A chiral (salen)Cr(III) complex is an efficient catalyst for the kinetic resolution of 2,2-disubstituted epoxides. The catalyst thus used was azido[2.2'-(1R,2R)-1,2-cyclohexanediylibis[(nitrilo- $\kappa$ N)methylidyne]]bis[4,6-bis(1,1-dimethylethyl)phenolato- $\kappa$ O](2-)chromium. The scope and limitations of this method are described.

RE.CNT 21 THERE ARE 21 CITED REFERENCES AVAILABLE FOR THIS RECORD  
 ALL CITATIONS AVAILABLE IN THE RE FORMAT

L11 ANSWER 11 OF 18 CAPLUS COPYRIGHT 2004 ACS on STN  
 AN 1999:6421 CAPLUS  
 DN 130:196334

TI Epoxide hydrolases and their synthetic applications  
 AU Orru, Romano V. A.; Archelas, Alain; Furstoss, Roland; Faber, Kurt  
 CS Institute of Organic Chemistry, Graz University of Technology, Graz, A-8010, Austria  
 SO Advances in Biochemical Engineering/Biotechnology (1999), 63(Biotransformations), 145-167  
 CODEN: ABEBOZ; ISSN: 0724-6145  
 PB Springer-Verlag  
 DT Journal: General Review  
 LA English  
 AB Review with 103 refs. Chiral epoxides and 1,2-diols, which are central building blocks for the asym. synthesis of bioactive compds., can be obtained by using enzymes, i.e. epoxide hydrolases, which catalyze the enantioselective hydrolysis of epoxides. These biocatalysts have recently been found to be more widely distributed in fungi and bacteria than previously expected. Sufficient sources from bacteria, such as Rhodococcus and Nocardia spp., or fungi, such as Aspergillus and Beauveria spp., have now been identified. The reaction proceeds via an SN2-specific opening of the epoxide, leading to the formation of the corresponding trans-configured 1,2-diol. For the resolution of racemic monosubstituted and 2,2- or 2,3-disubstituted substrates, various fungi and bacteria have been shown to possess excellent enantioselectivities. Addnl. different methods, which lead to the formation of the optically pure product diol in a chemical yield far beyond the 50% mark (which is intrinsic to classic kinetic resolns.), are discussed. In addition, the use of non-natural nucleophiles such as azides or amines provides access to enantiomerically enriched vicinal azido- and amino-alcs. The synthetic potential of these enzymes for asym. synthesis is illustrated with recent examples, describing the preparation of some biol. active mols.

RE.CNT 102 THERE ARE 102 CITED REFERENCES AVAILABLE FOR THIS RECORD  
 ALL CITATIONS AVAILABLE IN THE RE FORMAT

L11 ANSWER 12 OF 18 CAPLUS COPYRIGHT 2004 ACS on STN  
 AN 1996:668537 CAPLUS  
 DN 126:8027

TI Dynamic kinetic resolution of epichlorohydrin via enantioselective catalytic ring opening with TMSN3. Practical synthesis of aryl oxazolidinone antibacterial agents

AU Schaus, Scott E.; Jacobsen, Eric N.

CS Dep. Chem. Chem. Biol., Harvard Univ., Cambridge, MA, 02138, USA

SO Tetrahedron Letters (1995), 37(44), 7937-7940

CODEN: TELEAY; ISSN: 0040-4039

PB Elsevier

DT Journal

LA English

OS CASREACT 126:8027

AB The dynamic kinetic resolution of racemic epichlorohydrin has been achieved via enantioselective asym. ring opening with TMSN3 catalyzed by the (salen) Cr(III)N3 complex 1. The resulting 3-azido-1-chloro-2-trimethylsiloxypropane product was obtained in high enantiomeric purity and incorporated into the synthesis of U-100592, a representative from a class of highly-promising aryl oxazolidinone antibacterial agents.

L11 ANSWER 13 OF 18 CAPLUS COPYRIGHT 2004 ACS on STN  
 AN 1996:435229 CAPLUS  
 DN 125:194962

TI Kinetic Resolution of Terminal Epoxides via Highly Regioselective and Enantioselective Ring Opening with TMSN3. An Efficient, Catalytic Route to 1,2-Amino Alcohols

AU Larrow, Jay F.; Schaus, Scott E.; Jacobsen, Eric N.

CS Department of Chemistry and Chemical Biology, Harvard University, Cambridge, MA, 02138, USA

SO Journal of the American Chemical Society (1996), 118(31), 7420-7421

CODEN: JACSAT; ISSN: 0002-7863

PB American Chemical Society

DT Journal

LA English

OS CASREACT 125:194962

AB The (salen)Cr-catalyzed asym. epoxide ring opening reaction has been applied to the kinetic resolution of racemic terminal epoxides to provide 1-azido-2-trimethylsiloxyalkanes in 89-98% enantiomeric excess. The products are obtained in high yields and in excellent, often absolute, regiochem. purity. Epoxides bearing unbranched alkyl substituents were found to undergo kinetic resoln with highest efficiency, with *k*<sub>rel</sub> values well in excess of 100 for these substrates. The reaction also showed good functional group compatibility, with epoxides bearing chloride, alkoxide, and even Lewis basic cyano substituents displaying clean and highly enantioselective reactions. The utility of the ring-opened products as precursors to 1,2-amino alcs. was demonstrated by the synthesis of (S)-propranolol, a well-known antihypertensive agent, and of (R)-9-[2-(phosphonomethoxy)propyl]adenine, a compound recently shown to display prophylactic activity against SIV infection.

L11 ANSWER 14 OF 18 CAPLUS COPYRIGHT 2004 ACS on STN  
 AN 1995:569019 CAPLUS  
 DN 123:82537

TI Highly Enantioselective Ring Opening of Epoxides Catalyzed by (salen)Cr(III) Complexes

AU Martinez, Luis E.; Leighton, James L.; Carsten, Douglas H.; Jacobsen, Eric N.

CS Department of Chemistry, Harvard University, Cambridge, MA, 02138, USA

SO Journal of the American Chemical Society (1995), 117(21), 5897-8

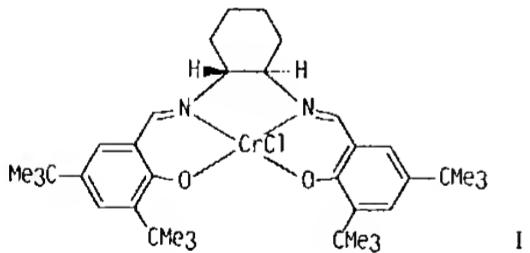
CODEN: JACSAT; ISSN: 0002-7863

PB American Chemical Society

DT Journal

LA English

GI



AB The chiral (salen)Cr complex I is a highly effective catalyst for the enantioselective ring-opening of epoxides with Me3SiN3. In the presence of 2 mol % I, a variety of both functionalized and unfunctionalized meso epoxides were converted to their corresponding azido silyl ethers with ee's 81-98%. Kinetic resolns. of styrene oxide and epichlorohydrin were also accomplished with the same catalyst system. In addition, the ring-opening of meso epoxides proceeds cleanly in the absence of solvent and with undiminished enantioselectivity. Removal of product by distillation permitted the recovery of a catalyst that could be reused repeatedly in the asym. ring-opening reaction with enhanced reactivity yet identical enantioselectivity relative to I. This solvent-free reaction constitutes an example of an asym. catalytic process that generates product with high ee and the highest possible volumetric productivity, producing no waste whatsoever.

L11 ANSWER 15 OF 18 CAPLUS COPYRIGHT 2004 ACS on STN  
 AN 1993:495235 CAPLUS  
 DN 119:95235

TI Antibody-catalyzed enantioselective epoxide hydrolysis

AU Sinha, Subhash C.; Keinan, Ehud; Reymond, Jean Louis

CS Dep. Chem., Technion-Israel Inst. Technol., Haifa, 32000, Israel

SO Journal of the American Chemical Society (1993), 115(11), 4893-4

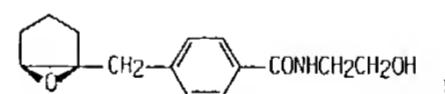
CODEN: JACSAT; ISSN: 0002-7863

DT Journal

LA English

OS CASREACT 119:95235

GI



AB A monoclonal antibody catalyzed the acidic hydrolysis of epoxides to trans diols. This enzyme-like catalysis is evident from the Michaelis-Menten kinetics with multiple turnovers. The pH-rate profiles suggest that these are acid-catalyzed reactions, where epoxides normally open at the more substituted carbon. The competing reaction with nucleophiles, e.g., chloride, azide, aminoethanol, mercaptoethanol (all found to attack preferentially at the less substituted carbon atom), is not catalyzed by this antibody. A preparative scale hydrolysis of racemic epoxide I produces the trans diol with enantioselectivity of >98%. By contrast, both enantiomers of a smaller substrate are equally reactive with this catalytic antibody. These observations highlight the importance of secondary interactions between substrate and antibody and suggest that such interactions are a necessary feature to be built in to obtain efficient, enantioselective antibody catalysts.

L11 ANSWER 16 OF 18 CAPLUS COPYRIGHT 2004 ACS on STN  
 AN 1991:247627 CAPLUS  
 DN 114:247627

TI  $\alpha$ -Amino aldehyde equivalents as substrates for rabbit muscle aldolase: synthesis of 1,4-dideoxy-D-arabinitol and 2(R),5(R)-bis(hydroxymethyl)-3(R),4(R)-dihydroxypyrrrolidine

AU Hung, Rebecca R.; Straub, Julie Ann; Whitesides, George M.

CS Dep. Chem., Harvard Univ., Cambridge, MA, 02138, USA

SO Journal of Organic Chemistry (1991), 56(12), 3849-55

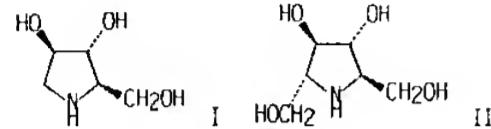
CODEN: JOCEAH; ISSN: 0022-3263

DT Journal

LA English

OS CASREACT 114:247627

GI



AB This work examined the application of rabbit muscle aldolase (RAMA) to stereospecific carbon-carbon bond formation in the preparation of carbohydrates containing amino groups. Several  $\alpha$ -amino aldehyde equivs. were evaluated as substrates for RAMA and for their synthetic utility in transformations following the aldol reaction. This methodol. is illustrated by the syntheses of the pyrrolidine alkaloids 1,4-dideoxy-1,4-imino-D-arabinitol (I) and 2(R),5(R)-bis(hydroxymethyl)-3(R),4(R)-dihydroxypyrrrolidine (II). The kinetic resoln. of racemic aldehydes by RAMA and mild methods for transforming the amino equivs. into the desired amines are discussed briefly.

L11 ANSWER 17 OF 18 CAPLUS COPYRIGHT 2004 ACS on STN  
 AN 1990:514960 CAPLUS  
 DN 113:114960

TI Enzymes in organic synthesis: synthesis of highly enantiomerically pure 1,2-epoxy aldehydes, epoxy alcohols, thiirane, aziridine, and glyceraldehyde 3-phosphate

AU Pederson, Richard L.; Liu, Kevin K. C.; Rutan, James F.; Chen, Lihren; Wong, Chi Huey

CS Dep. Chem., Res. Inst. Scripps Clin., La Jolla, CA, 92037, USA

SO Journal of Organic Chemistry (1990), 55(16), 4897-901

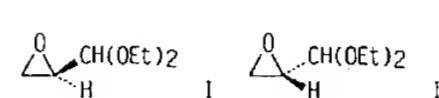
CODEN: JOCEAH; ISSN: 0022-3263

DT Journal

LA English

OS CASREACT 113:114960

GI



AB An enzymic procedure for the synthesis of (R)- and (S)-glycidaldehyde di-Et acetal (I and II) is described. (±)-C1CH2CH(OAc)CH(OEt)2 was enantioselectively hydrolyzed by LP-80 lipase to give (S)-C1CH2CH(OH)CH(OEt)2 and (R)-C1CH2CH(OAc)CH(OEt)2, both in >95% calculated yield and >95% enantiomeric excess (ee). Both products were subsequently converted to epoxides I and II resp. Resolns. of (±)-C1CH2CH(OAc)CH2OCH2Ph and CH2CH(OAc)CH2OCH2CH(OAc)CH2O3SC6H4Me-p were similarly carried out to give the corresponding optically active 2-hydroxy and 2-acetoxy derivs. in 90% and >95% ee. These products were subsequently converted to the corresponding 1,2-epoxides. Nucleophilic opening of epoxide I was exemplified by the syntheses of (R)-N3CH2CH(OH)CH(OEt)2 and D-glyceraldehyde 3-phosphate. Conversion of the chiral epoxides to thiiranes and aziridines was also described.

L11 ANSWER 18 OF 18 CAPLUS COPYRIGHT 2004 ACS on STN  
 AN 1989:154053 CAPLUS  
 DN 110:154053

TI Metal(II) d-tartrates catalyzed asymmetric ring opening of oxiranes with various nucleophiles

AU Yamashita, Hiroyuki

CS Cent. Res. Inst., Mitsui Toatsu Chem., Inc., Yokohama, 247, Japan

SO Bulletin of the Chemical Society of Japan (1988), 61(4), 1213-20

CODEN: BCSJA8; ISSN: 0009-2673

DT Journal

LA English

OS CASREACT 110:154053

AB The asym. ring opening of meso-2,3-disubstituted oxiranes with thiols, PhNH2, and Me3SiN3 (I) was studied by the use of metal(II) d-tartrates as heterogeneous chiral Lewis acid catalysts. The enantioselectivity varied widely with the combination of oxirane, nucleophile, and metal(II) d-tartrate. Zn(II) d-tartrate gave the best enantioselectivity in the reactions of 1,2-epoxycyclohexane with 1-butanethiol, PhNH2, and I to afford the adducts in 85, 58, and 42% enantiomeric excess, resp. The kinetic resolution of racemic oxiranes with thiols catalyzed by Zn(II) d-tartrate was also studied.